

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 347 003
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **89201558.7**

(51) Int. Cl.⁴: **C10G 11/05 , C10G 45/64**

(22) Date of filing: **14.06.89**

(30) Priority: **16.06.88 GB 8814293**
27.02.89 GB 8904409

(43) Date of publication of application:
20.12.89 Bulletin 89/51

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(71) Applicant: **SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.**
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

(72) Inventor: **Maxwell, Ian Ernst**
Badhuisweg 3
NL-1031 CM Amsterdam(NL)
Inventor: **van der Eijk JJohan Meindert**
Badhuisweg 3
NL-1031 CM Amsterdam(NL)
Inventor: **Biswas, Jaydeep**
Badhuisweg 3
NL-1031 CM Amsterdam(NL)

(74) Representative: **Aalbers, Onno et al**
P.O. Box 302
NL-2501 CH The Hague(NL)

(54) **Process for the conversion of a hydrocarbonaceous feedstock.**

(57) Process for the conversion of a hydrocarbonaceous feedstock having an end boiling point of at most 330 °C, which process comprises contacting the feedstock with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm at a temperature above 500 °C during less than 10 seconds.

EP 0 347 003 A1

PROCESS FOR THE CONVERSION OF A HYDROCARBONACEOUS FEEDSTOCK

The present invention relates to a process for the conversion of a hydrocarbonaceous feedstock.

In US-A-4,390,413 a process is described in which a hydrocarbonaceous feedstock is upgraded by contacting the feedstock with a ZSM-5 containing catalyst in a fixed bed reactor at a pressure below 14 bar, a temperature of 260 to 427 °C and a space velocity of 0.1 to 15 l/h. The feedstock must contain less than 5 ppmw of nitrogen-containing compounds, calculated as nitrogen. Although the feedstock exemplified is a gas oil, suitable feedstocks include hydrocarbons with a boiling range from 82 to 649 °C. The products include olefinic hydrocarbons, such as propene and butenes. This production of olefins is desirable, since they tend to be valuable products. The known process has the drawback that the feedstock must have been severely denitrified. This is necessary as the more nitrogenous feedstocks would deactivate the catalyst rapidly.

It has surprisingly been found that a comparatively high yield of olefins can be obtained, under less stringent conditions as regards nitrogen content, using certain zeolitic catalysts, at high temperature with a short contact time of the feedstock with the catalyst.

Accordingly, the present invention provides a process for the conversion of a hydrocarbonaceous feedstock having an end boiling point of at most 330 °C, which process comprises contacting the feedstock with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm, preferably 0.5 to 0.7 nm, at a temperature above 500 °C during less than 10 seconds.

The feedstock is contacted with the zeolitic catalyst for less than 10 seconds. Suitably, the minimum contact time is 0.1 second. Very good results are obtainable with a process in which the feedstock is contacted with the zeolitic catalyst during 0.2 to 6 seconds.

The surprising nature of the present invention is further illustrated by US-A-4,100,218, which describes a process for the preparation of LPG (saturated C₃₋₄-hydrocarbons) and gasoline starting from an olefinic stream, using a catalyst with a pore diameter of less than 0.7 nm. Since it was known that such zeolitic catalysts have activity to catalyze the conversion of olefins to saturated and aromatic hydrocarbons, it is surprising that in the present process olefins are produced and relatively little saturated gaseous hydrocarbon product is formed.

The temperature during the reaction is above 500 °C and preferably up to 900 °C. The temperature is preferably from 550 to 800 °C.

The zeolitic catalyst may comprise one or more zeolites with a pore diameter of from 0.3 to 0.7 nm. The catalyst suitably further comprises a refractory oxide that serves as binder material. Suitable refractory oxides include alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures thereof. Alumina is especially preferred. The weight ratio of refractory oxide and zeolite suitably ranges from 10:90 to 90:10, preferably from 50:50 to 85:15. The zeolitic catalyst preferably comprises as zeolite substantially only zeolites with a pore diameter of from 0.3 to 0.7 nm. Illustrative of the invention is the use of a zeolitic catalyst comprising a zeolite of pore diameter of 0.5 to 0.7 nm at a temperature above 500 °C and up to 750 °C.

The term zeolite in this specification is not to be regarded to comprise only crystalline aluminium silicates. The term also includes crystalline silica (silicalite), silicoaluminophosphates (SAPO), chromosilicates, gallium silicates, iron silicates, aluminium phosphates (ALPO), titanium aluminosilicates (TASO), boron silicates, titanium aluminophosphates (TAPO) and iron aluminosilicates. Examples of zeolites that may be used in the process of the invention and that have a pore diameter of 0.3 to 0.7 nm, include SAPO-4 and SAPO-11, which are described in US-A-4,440,871, ALPO-11, described in US-A-4,310,440, TAPO-11, described in US-A-4,500,651, TASO-45, described in EP-A-229,295, boron silicates, described in e.g. US-A-4,254,297, aluminium silicates like erionite, ferrierite, theta and the ZSM-type zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-23, and ZSM-38. Preferably the zeolite is selected from the group consisting of crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof. Suitable examples of crystalline metal silicates with ZSM-5 structure are aluminium, gallium, iron, scandium, rhodium and/or chromium silicates as described in e.g. GB-B-2,110,559.

After the preparation of the zeolites usually an amount of alkali metal oxide is present in the readily prepared zeolite. Preferably the amount of alkali metal is removed by methods known in the art, such as ion exchange, optionally followed by calcination, to yield the zeolite in its hydrogen form. Preferably, the zeolite used in the present process is substantially in its hydrogen form.

The pressure in the present process can be varied within wide ranges. It is, however, preferred that the pressure is such that at the prevailing temperature the feedstock is substantially in its gaseous phase or brought therein by contact with the catalyst. Then it is easier to achieve the short contact times

envisaged. Hence, the pressure is preferably relatively low. This can be advantageous since no expensive compressors and high-pressure vessels and other equipment is necessary. A suitable pressure range is from 1 to 10 bar. Subatmospheric pressures are possible, but not preferred. It can be economically advantageous to operate at atmospheric pressure. Other gaseous materials may be present during the conversion such as steam and/or nitrogen.

The present process is preferably carried out in a moving bed. The bed of catalyst may move upwards or downwards. When the bed moves upwards a process somewhat similar to a fluidized catalytic cracking process is obtained.

During the process some coke may be formed on the catalyst. Therefore, it would be advantageous to regenerate the catalyst. Preferably the catalyst is regenerated by subjecting it after having been contacted with the feedstock to a treatment with an oxidizing gas, such as air. A continuous regeneration, similar to the regeneration carried out in a fluidized catalytic cracking process, is especially preferred.

If the coke formation does not occur too high a rate it would be possible to arrange for a process in which the residence time of the catalyst particles in a reaction zone is longer than the residence time of the feedstock in the reaction zone. Of course, the contact time between feedstock and catalyst should be less than 10 seconds. The contact time generally corresponds with the residence time of the feedstock. Suitably the residence time of the catalyst is from 1 to 20 times the residence time of the feedstock.

While the catalyst/feedstock weight ratio is not critical, it is preferred that the weight ratio varies from 1 to 150 kg or more of catalyst per kg of feedstock. Preferably, the catalyst/feedstock weight ratio is from 20 to 120:1.

The feedstock which is to be converted in the present process comprises hydrocarbons which have an end boiling point of at most 330 °C. By this feature relatively light petroleum fractions, like naphtha and kerosine, are included. Preferably the feedstock has an initial boiling point of -45 °C. Suitable feedstocks include C₃-4-hydrocarbons (e.g. LPG), naphtha, gasoline fractions, kerosine fractions and mixtures thereof.

One of the advantages of the present invention over the process according to US-A-4,390,413 resides in the fact that a feedstock with a relatively high nitrogen content may be used with substantially no effect on the catalyst activity. Suitable feedstocks may have a nitrogen content of more than 25 ppmw, calculated as nitrogen. The feedstock may even have a nitrogen content of 100 to 1000 ppmw, calculated as nitrogen.

The present invention will be further illustrated by means of the following examples.

EXAMPLE 1

In a series of experiments a conversion process was carried out using as feedstock a C₅-7 hydrocarbon mixture with the following distribution:

isopentane	25.7 %wt
n-pentane	26.3 %wt
isohexane	0.3 %wt
n-hexane	23.4 %wt
isoheptane	0.8 %wt
n-heptane	23.5 %wt

It is observed that the boiling point of the compound with the highest boiling point is 98.5 °C.

The experiments were carried out in a down flow reactor in which co-currently a flow of feedstock and catalyst particles, having an average particle size of 74 micrometers, was passed downwards. The catalyst used comprised ZSM-5 in hydrogen form in an alumina matrix (weight ratio ZSM-5/alumina was 1:3). All experiments were carried out at atmospheric pressure. Further process conditions and the results of the experiments are indicated in Table 1 below.

In the table the sign "=" indicates olefinic unsaturation, and "C₅+" indicates hydrocarbon products with 5 or more carbon atoms that are not normal or iso-paraffinic.

TABLE 1

Experiment No.	1	2	3	4
Temperature, °C	400	500	500	550
Catalyst/oil ratio, kg/kg	8.0	5.8	30.1	34.9
Contact time, s	2.0	2.0	2.0	2.0
Product, %wt				
H ₂	0.0	0.1	0.1	0.2
C ₁	0.0	0.2	0.3	1.2
C ₂	0.2	2.4	3.3	7.5
C ₃	1.9	7.0	10.6	14.1
C ₄	2.3	4.6	7.0	7.8
i-C ₅	26.3	24.9	24.5	22.7
n-C ₅	25.8	23.9	22.7	22.1
i-C ₆	0.4	0.3	0.3	0.2
n-C ₆	20.6	18.1	14.7	12.3
i-C ₇	0.8	0.5	0.5	0.3
n-C ₇	20.0	16.3	12.9	7.2
C ₅	0.9	0.8	1.1	1.4
coke on catalyst	0.8	0.9	2.0	3.0
Unsaturation				
C ₂ = C ₂	1.7	1.8	1.9	1.7
C ₃ = C ₃	0.8	1.1	1.0	1.5
C ₄ = C ₄	0.5	1.3	1.1	1.9

From the above results it is apparent that n-paraffins are preferentially cracked and yield gaseous products which comprise a significant amount of olefins, especially at temperatures above 500 °C. Above 500 °C it will be seen that there is a markedly increased C₃ and C₄ olefin/paraffin ratio and an overall increased conversion to lower olefins. The resulting liquid product has a higher iso/normal-paraffin ratio than the starting mixture, so that, additionally, the octane number and hence the quality of the liquid product as a gasoline has been enhanced.

EXAMPLE 2

A further conversion process was carried out using as feedstock a C₅-₁₀ hydrocarbon mixture with the following distribution (as %w on feed):

paraffins	55.9
naphthenes	32.9
aromatics	11.3
IBP	50 °C
FBP	199 °C
50%	119 °C

The experiment was carried out at atmospheric pressure using the reactor and catalyst described in Example 1. Further process conditions and the results of the experiments are indicated in Table 2 below. In the table the sign "=" indicates olefinic unsaturation.

TABLE 2

Process conditions:	
Reactor temperature, °C	580
Catalyst/oil ratio, g/g	112
Contact time, s	1.9
Product, %w on feed	
C ₁	1.4
C ₂	1.7
C ₂ ⁼	7.4
C ₃	4.0
C ₃ ⁼	16.5
C ₄	2.3
C ₄ ⁼	8.0
C ₅ -221 °C	50.5
221-370 °C	0.8
Coke	7.0

It will be noted that a high yield of a predominantly olefinic C₂-4 product is obtained.

Claims

1. A process for the conversion of a hydrocarbonaceous feedstock having an end boiling point of at most 330 °C, which process comprises contacting the feedstock with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm at a temperature above 500 °C during less than 10 seconds.

2. A process according to claim 1, in which the feedstock is contacted with the zeolitic catalyst during 0.2 to 6 seconds.

3. A process according to claim 1 or 2, in which the temperature is from 500 to 900 °C.

4. A process according to claim 3, in which the temperature is from 550 to 800 °C.

5. A process according to any one of claims 1 to 4, in which the zeolitic catalyst comprises as zeolites substantially only zeolites with a pore diameter of from 0.3 to 0.7 nm.

6. A process according to any one of the preceding claims wherein the zeolite has a pore diameter of 0.5 to 0.7 nm and the temperature is up to 750 °C.

7. A process according to any one of claims 1 to 6, in which the zeolite is selected from the group consisting of crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof.

8. Process according to any one of claims 1 to 7, in which the zeolite is in substantially in its hydrogen form.

9. A process according to any one of claims 1 to 8, in which the pressure is from 1 to 10 bar.

10. A process according to any one of claims 1 to 9, in which the catalyst/feedstock weight ratio is from 1 to 150:1, preferably from 20 to 120:1.

11. A process according to any one of claims 1 to 10, which is carried out in a moving bed of catalyst.

12. A process according to any one of claims 1 to 11, in which the feedstock has an initial boiling point of at least -45 °C.

13. A process according to claim 12, in which the feedstock comprises C₃-4-hydrocarbons, naphtha, gasoline, kerosine or mixtures thereof.

14. A process according to claim 1, substantially as described hereinbefore with reference to the Examples.

15. A hydrocarbonaceous product, or a fraction thereof, when obtained by the process of any one of the preceding claims.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 20 1558

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-A-3 856 659 (OWEN) * Abstract; columns 2,5; claims 1-9 *	1-15	C 10 G 11/05 C 10 G 45/64
Y	US-A-4 218 344 (VASALOS) * Abstract; columns 4,5,9; claims 1-5 *	1-15	
A	US-A-3 886 060 (OWEN) * Abstract; columns 1-3; claims 1-12 *	1-15	
A	US-A-3 140 322 (FRILETTE et al.)		
D,A	US-A-4 310 440 (WILSON et al.)		
D,A	US-A-4 390 413 (O'REAR et al.)		
D,A	US-A-4 100 218 (CHEN et al.)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11-09-1989	Examiner LO CONTE C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPD FORM 1503 03.82 (P0401)